PATENT ABSTRACTS OF JAPAN

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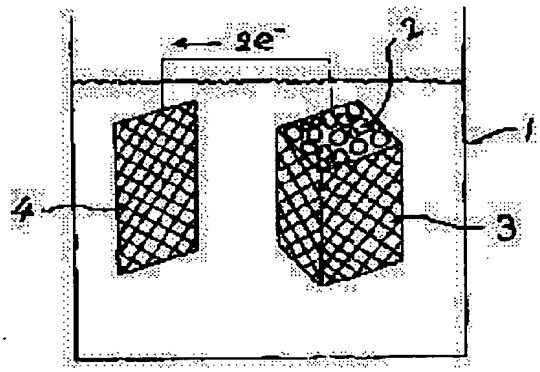
(54) COPPER DISSOLUTION TANK IN COPPER PLATING APPARATUS

(57)Abstract:
PROBLEM TO BE SOLVED: To more promote the dissolution of copper in a copper dissolution tank equipped for a copper plating apparatus compared with the conventional case.
SOLUTION: In a copper dissolution tank 1 equipped for a copper plating apparatus having an insoluble anode and charged with a tervalent iron- containing solution, a piece 4 consisting of a material having catalystic activity higher than that of titanium such as iridium oxide is disposed for the copper dissolution tank in addition to a storing body 3 stored with a copper material 2, and the iridium oxide piece is connected with the copper material.



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CLAIMS

[Claim(s)]
[Claim 1] Copper dissolver characterized by making the reduction reaction of trivalent iron ion perform on the front face of an ingredient with catalytic activity higher than titanium in the copper dissolver which was attached to copper-plating equipment with an insolubility anode, and put in the trivalent iron ion content solution.
[Claim 2] Copper dissolver according to claim 1 characterized by arranging the piece which becomes with an ingredient with catalytic activity higher than titanium in [other than a copper material hold container] copper dissolver, and connecting the ingredient piece concerned with copper material.
[Claim 3] Copper dissolver according to claim 1 characterized by constituting a part or all of copper dissolver from an ingredient with catalytic activity higher than titanium, and connecting copper material to the ingredient concerned.
[Claim 4] Copper dissolver according to claim 1 characterized by arranging the piece which comes with an ingredient with catalytic activity higher than titanium between the copper material held in the container, and an ingredient piece and copper material concerned contacting.
[Claim 5] Copper dissolver according to claim 1 characterized by coating a copper material hold container with an ingredient with catalytic activity higher than titanium.
[Claim 6] Copper dissolver given in any 1 term of claims 1-5 characterized by being chosen from the group to which the above-mentioned ingredient becomes a periodic table's metals, those alloys, and those oxide lists of the 8th group from C alloy.
[Claim 7] Copper dissolver according to claim 2 or 4 characterized by the above-mentioned ingredient piece being a mesh-like plate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the promotion of supply of the copper ion in the electrolytic copper plating equipment which uses an insolubility anode (anode plate).
[0002]
[Description of the Prior Art] Since metal copper was deposited on the printed circuit board which makes cathode in giving copper plating to a printed circuit board etc., in order to fill up the copper consumed there, the dissolution of copper was made in ancient times in the anode plate. However, when the acid copper content electrolytic solution like a copper sulfate bath or a HOUFUTSU-ized copper bath performs copper plating, using an insolubility anode as an anode plate, in an anode plate side, water is disassembled and oxygen occurs on an anode plate front face. Formation of an organic reaction product which controls the reaction on the front face of an anode plate in connection with it, or passivates the front face concerned takes place. This can affect surface distribution in printed circuit board cathode.
[0003] Then, on the occasion of copper-plating processing, it is proposed that it is made to perform the alternative-reaction to oxygen evolution. One of them is use of the electrolytic solution containing sufficient quantity of divalent iron ion, in order to obtain all electrons required for an anodic reaction from the oxidation to trivalent iron ion (Fe3+) from divalent iron ion (Fe2+).
[0004] When using such the electrolytic solution and an insolubility anode for copper plating, the copper dissolver which put in the trivalent iron ion content solution for the supplement to the copper ion by which deposit consumption is carried out is prepared. This copper dissolver is made to correspond to the amount of the copper deposit on the substrate which is a cathode reaction, and generates a copper ion and an electron from copper material. Copper material can have various configurations and is held in the container which are a rod-like structure and a minor diameter solid sphere, for example, becomes by the titanium this copper material excelled [titanium] in the chemistry resistance over plating liquid. [two or more] The cathode reaction in a cell is Cu2++2e—>Cu0 here. (1)
Moreover, an anodic reaction is Fe2+->Fe3++e-. (2)
It comes out. Moreover, supply of the copper ion in copper dissolver is performed by the next reaction.
Cu0+2Fe3+->Cu2++2Fe2+ (3)
[0005]
[Problem(s) to be Solved by the Invention] As mentioned above, copper ion supply of copper dissolver is usually based on the approach of carrying out generation supply of the copper ion from the copper material held in the container made from titanium.
[0006] This copper lytic reaction (3) advances in the combination of the following oxidation reduction reactions in a trivalent iron ion content solution.
Cu0 ->Cu2++2e- (4)
2Fe(s)3++e—>Fe2+ (5)
[0007] The rate-determining step of this oxidation reduction reaction is the divalent reduction reaction of the trivalent iron ion shown in (5) types. The rate of this reduction reaction has a low reaction by the titanium which is the material of the basket which is greatly dependent on the catalytic activity of the metal which runs on that front face, and holds copper or copper material. Moreover, the reaction of (5) types is a diffusion limitation, and since it depends also on the stirring conditions near the copper material front face strongly, it is necessary to fully stir. Therefore, with the configuration in which copper material is put into the container made from titanium, and a copper ion is dissolved, there was a case where the dissolution of the copper in copper dissolver did not fully progress.
[0008] So, this invention makes it a technical problem to promote conventionally the dissolution of the copper in the copper dissolver attached to copper-plating equipment.
[0009]
[Means for Solving the Problem] According to this invention, the above-mentioned technical problem was solved in the copper dissolver which was attached to copper-plating equipment with an insolubility anode, and put in the trivalent iron ion content solution by making a copper reduction reaction perform on the front face of an ingredient with catalytic activity higher than titanium.
[0010] It is suitable to arrange the piece which becomes with an ingredient with catalytic activity higher than titanium in [other than a copper material hold container] copper dissolver, and to connect the ingredient piece concerned with copper material. Moreover, a part or all of copper dissolver may be constituted from an ingredient with catalytic activity higher than titanium, and copper material may be connected to this. Moreover, it is convenient, even if it contacts an ingredient piece and copper material concerned, or it arranges the piece which becomes with the high ingredient of catalytic activity, and an ingredient with catalytic activity higher than titanium constitutes the copper material hold container itself from titanium between the copper material held in the container or it coats a container front face with the ingredient concerned.
[0011] It is desirable to be chosen from the group to which the above-mentioned ingredient becomes a periodic table's metals, those alloys, and those oxide lists of the 8th group from C alloy. For example, they are IrO2, Pt, Rh, Pd, Pt-Ir, etc. It is convenient if an ingredient piece is a mesh-like plate.
[0012]

[Embodiment of the Invention] It explains based on the example which shows the detail of this invention in drawing. In addition, the body of copper-plating equipment with which the copper dissolver concerned should be attached does not have a well-known thing and the changing place conventionally, and omits illustration and a publication for simplification of explanation.
[0013] The configuration of the 1st copper dissolver is shown in drawing 1 . In drawing 1 , the plate 4 of the shape of a mesh which becomes with oxidization iridium is connected to the titanium basket 3 which held the copper ball object 2 in the copper dissolver 1. By such configuration, the electron generated with the copper dissolution can flow to the oxidization iridium plate 4, and can promote the reduction reaction of trivalent iron ion (Fe3+) using the high catalytic activity of oxidization iridium. Moreover, by making the configuration of the oxidization iridium plate 4 into the shape of a mesh, it also becomes possible to fully secure stirring of a solution.
[0014] The balanced Fe3+ concentration the case of a configuration of having only held the copper ball object in the titanium basket and in a configuration of having connected the mesh-like oxidization iridium plate to the titanium basket is shown in Table 1. The surface area of 27mm and this copper ball object of the diameter of the copper ball object used here is 2 3069cm. One configuration of an oxidization iridium plate has been arranged by each side of the titanium basket in copper dissolver by 20cm long and 10cm wide, respectively, and was connected to the titanium basket. Moreover, the amount of circulating flow of 20.9l. and plating liquid of the amount of all plating liquid is 90l./o'clock. When an oxidization iridium plate is connected, Fe3+ concentration is low and it means that the copper lytic reaction according to the above-mentioned reaction formula (3) is promoting this.
[0015]
[Table 1]

溶解槽の構成	平衡Ｆｅ$^{3+}$濃度（ｇ／ﾘｯﾄﾙ）
チタンバスケットのみ使用	５．７
酸化イリジウム板併用	４．５

[0016] The configuration of the 2nd copper dissolver 10 is shown in drawing 2 . It arranges so that the mesh-like oxidization iridium plate 4 may be inserted between the copper ball objects 2 of the titanium basket 3. By considering as such a configuration, the reduction reaction of Fe3+ will progress on the oxidization iridium plate 4 in the titanium basket 3.
[0017] According to the 2nd operation gestalt, since an oxidization iridium plate is not formed out of a titanium basket, it becomes possible for an oxidization iridium plate and the connection for titanium basket connection to be unnecessary, and for a configuration to be simplified, and to make copper dissolver small.
[0018] Moreover, in the case of this operation gestalt, as a copper material hold container slack basket, it is not a thing made from titanium and Fe3+ reduction reactions, such as Teflon (trademark), may be made of the ingredient which cannot advance. Moreover, since an oxidization iridium plate is indirectly connected with copper material through a basket also with the 1st operation gestalt, as long as it connects the foil and an oxidization iridium plate with copper material directly, a basket may consist of Teflons etc.
[0019] In addition, it is possible, replacing with the two above-mentioned examples, and coating etc. carrying out a part or all of the configuration which forms the basket itself with oxidization iridium, or coats it, or copper dissolver with oxidization iridium, and making the reduction reaction of trivalent iron ion perform in the part naturally.
[0020]
[Effect of the Invention] As explained above, according to this invention, the reduction reaction to Fe2of Fe3++ can be made to perform on an ingredient with catalytic activity higher than titanium, and it becomes possible to promote the copper dissolution only from the case of having put in copper material into the container made from titanium.
[0021] The ingredient which has high catalytic activity for the reduction reaction to the divalent iron ion of trivalent iron ion is common into the ingredient which has high catalytic activity in the electrolytic oxidation to the trivalent iron ion of divalent iron ion. Therefore, it is chosen from the group to which it becomes the point to which to choose the ingredient in which a good property is shown in the measurement result of the latter catalytic activity, and it becomes a periodic table's metals, those alloys, and those oxide lists of the 8th group from C alloy, and oxidization iridium and platinum are especially desirable.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the conceptual block diagram of the copper dissolver concerning the 1st example of this invention.
[Drawing 2] It is the conceptual block diagram of the copper dissolver concerning the 2nd example of this invention.
[Description of Notations]
1 Ten Copper dissolver
2 Copper Material
3 Titanium Basket
4 Oxidization Iridium Plate

[Translation done.]